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Narrow rim CMPO/adamantylcalix[4]arenes for the extraction of lanthanides and actinides

Ivan Vatsouro [a], Alina Serebryannikova [a], Leyong Wang [b], Véronique Hubscher-Bruder [c,d], Elvira Shokova [a], Michael Bolte [e], Françoise Arnaud-Neu [c,d], Volker Böhmer [b], Vladimir Kovalev [a,*]

[a] Laboratory of Macrocyclic Receptors, Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russia
[b] Abteilung Lehramt Chemie, Fachbereich Chemie, Pharmazie und Geowissenschaften, Johannes Gutenberg Universität, 55099 Mainz, Germany
[c] Université de Strasbourg, IPHC, 25 rue Becquerel, 67087 Strasbourg, France
[d] CNRS, UMR 7178, 67037 Strasbourg, France
[e] Institut für Anorganische Chemie, Johann Wolfgang Goethe-Universität, 60439 Frankfurt/Main, Germany

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ABSTRACT

Six *p*-(1-adamantyl)calix[4]arenes **7**, **8** with four differently attached diphenyl-carbamoylmethyl phosphine oxide (CMPO) functions at the narrow rim were synthesized. This series was extended by adamantylcalix[4]arenes with two CMPO and two ester, acid or (diethylphosphono)acetylamino groups. Structures of new compounds were proved by NMR, mass-spectrometry and a single-crystal X-ray analysis for the intermediate di-phthalimide $\mathbf{10_3}$. The extraction studies towards selected lanthanides and thorium showed that the ligands **7** surpassed the corresponding *p*-H, *p*-*tert*-butyl and *p*-*tert*-octyl analogues **3**–**5** in lanthanide extraction while thorium was extracted with the same or lesser extent. For the lanthanide extraction $D_{Ln}(\mathbf{7_4}) > D_{Ln}(\mathbf{7_3}) \approx D_{Ln}(\mathbf{7_2})$, which follows the order established earlier for ligands **3**–**5**. Among the tetra-CMPO derivatives of type **8**, the ligand $\mathbf{8_{3/4}}$ was the best extractant for which the D_{Ln} and D_{Th} values were comparable with those for $\mathbf{7_4}$.

1. Introduction

Nuclear waste treatment is currently an important task aimed at reducing the amount and activity of toxic nuclides to be stored. The removal of uranium and plutonium from irradiated nuclear fuel (industrial PUREX process)[1] results, unfortunately, in a significant volume of highly acidic solutions containing numerous long-lived radionuclides. Several industrial extraction processes have been developed for the reprocessing of these acidic solutions; the TRUEX process utilizing CMPO ((*N*,*N*-diisobutylcarbamoylmethyl)octylphenylphosphine oxide, **1**, Scheme 1) as an extractant is one of them.[2,3] Although the extraction level provided by CMPO-like ligands is high, more effective and much more An/Ln selective ligands are necessary to meet the current ecological requirements.

As the extracted complex contains three molecules of bidentate CMPO per cation,[4,5] a significant improvement of the extraction ability of ligands can be achieved by pre-organization of several CMPO-like groups on a common platform,[6] including calixarenes, which have been studied in a broad range of structural variations. Thus, four CMPO-like groups were grafted onto the wide or narrow rim of *cone* calix[4]arene scaffold to get ligands of types **2**–**5**, which are highly efficient for *f*-element extraction.[7–12] The first CMPO/calixarenes rigidified in the 1,3-*alternate* conformation have also been recently reported.[13]

In line with our research in adamantylcalix[4]arene chemistry we have created efficient actinide/lanthanide extractants of type **6** in which the adamantane units served as linkers between calixarene core and CMPO groups.[14,15] We have also established previously a high extraction ability of the *p*-(1-adamantyl)calixarenes with four CMPO-groups attached to the narrow rim identically (compounds **7**) or in an alternating fashion (compounds **8**) towards 'hot' ^{241}Am and ^{152}Eu.[15] Here we describe in detail the syntheses of **7** and **8**, and related compounds with mixed functionalities obtained both by selective alkylation of the narrow rim of adamantylcalix[4]arene and an amine protection/deprotection route. In order to evaluate the influence of the adamantane units at the wide rim and the CMPO attachment mode at the narrow rim of calix[4]arenes onto the complexation properties of the ligands, a series of extraction experiments with selected lanthanides and thorium were conducted under conditions similar to those used earlier for the study of compounds **3**–**5**.

* Corresponding author. Tel.: +7 495 939 1302; fax: +7 495 932 8846; e-mail address: kovalev@petrol.chem.msu.ru (V. Kovalev).

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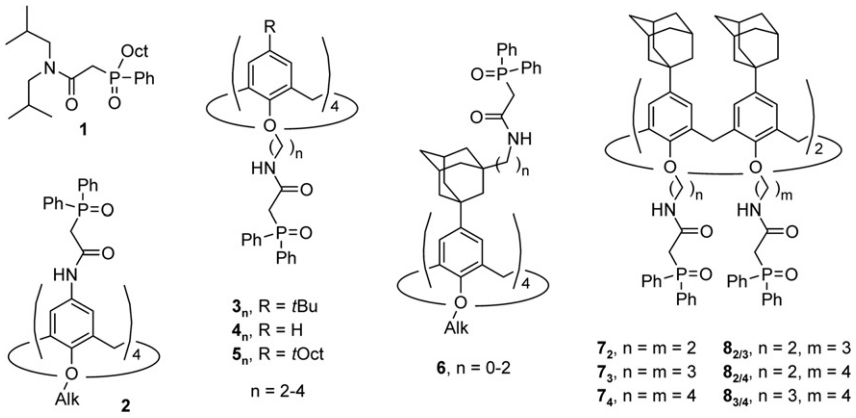


Scheme 1. CMPO-ligands used for discussions (**1**–**6**) and studied (**7**–**8**).

2. Results and discussion

2.1. Synthesis

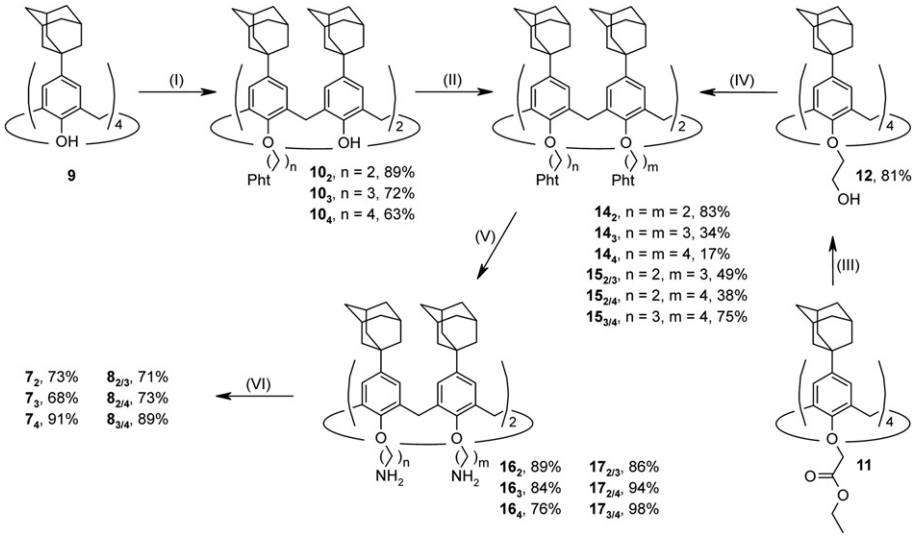
The narrow rim CMPO-derivatives of calixarenes appear to be easily available through the alkylation of the parent macrocycles with ω-bromoalkylphthalimides followed by hydrolysis and acylation with the phosphorous-containing active ester.[10] Nevertheless, the direct exhaustive alkylation of (1-adamantyl)calix[4]arene **9** with 3-bromopropyl- and 4-bromobutylphthalimides using NaH as the base did not lead to the desired tetra-alkylated calixarenes as the major products, while giving a complex mixture of compounds, that could be explained by the solubility issues. (The use of 2-bromoethyl phthalimide under these conditions was proved to be unsuccessful due to rapid HBr elimination from the reagent.[10]) Thus, other methods were required for the synthesis of the target calixarene derivatives.

The two-step alkylation of calixarenes can decrease the number of possible side-products compared with the exhaustive reaction and also expand the range of tetra-alkyl derivatives, which can be obtained when two different reagents are used. Adamantylcalix[4]arenes **10** were obtained from calixarene **9** in good yield by the selective alkylation with 3-bromopropyl- and 4-bromobutylphthalimides using K_2CO_3 as the base or by the selective Mitsunobu reaction with 2-hydroxyethylphthalimide[16] in the case of $\mathbf{10_2}$ (Scheme 2).

Upon re-crystallization from chloroform/methanol, colourless needles of $\mathbf{10_3}$ suitable for single-crystal X-ray analysis were obtained. In the crystalline state $\mathbf{10_3}$ possesses a *pinched cone* conformation stabilized with hydrogen bonds between OH groups and ether oxygen atoms (Fig. 1), and forms infinite chains due to the inclusion of one phthalimide group into the cavity of the neighbouring molecule (Fig. 2). The crystal data for $\mathbf{10_3}$ are collected in Table 1.

The further NaH-promoted alkylation of **10** gave the desired *cone* tetra-phthalimides $\mathbf{14_3}$, $\mathbf{14_4}$ and **15** in moderate to good yield. In the cases when the same alkylating reagent was used in both steps, the tri-phthalimides $\mathbf{13_3}$ and $\mathbf{13_4}$ were also obtained in 35 and 9% yield, respectively.

As the Mitsunobu condensation of (thia)calix[4]arenes with 2-hydroxyethylphthalimide is strongly selective, no tetra-alkylated products can be obtained by this method even when a large excess of reagents is used.[16,17] Assuming the mentioned difficulties with the $BrCH_2CH_2Pht$/NaH/DMF alkylation also in the case of $\mathbf{10_2}$, the synthesis of tetraphthalimide $\mathbf{14_2}$ required a completely different approach. In early examples, the aminoethyl functionalities have been introduced to the narrow rim of *p-tert*-butylcalix[4]arene by the tetraester reduction, tosylation of the tetrol, followed by reaction with NaN_3 and reduction.[10,18] The one step shorter and more efficient route was used for the modification of adamantylcalix[4]arene: the tetraester **11**[19] was reduced, and the resultant tetrol **12**



Scheme 2. Synthesis of tetra-CMPO derivatives **7** and **8**. (I) for n=2: $HO(CH_2)_2Pht$, Ph_3P, DIAD, THF; for n=3, 4: $Br(CH_2)_nPht$, K_2CO_3, CH_3CN; (II) for m=3, 4: $Br(CH_2)_mPht$, NaH, DMF; (III) $LiAlH_4$, THF; (IV) for n=m=2: HPht, Ph_3P, DEAD, THF; (V) $N_2H_4 \cdot H_2O$, EtOH/THF; (VI) *p*-nitrophenyl (diphenylphosphoryl)acetate, Et_3N, $CHCl_3$ or toluene.

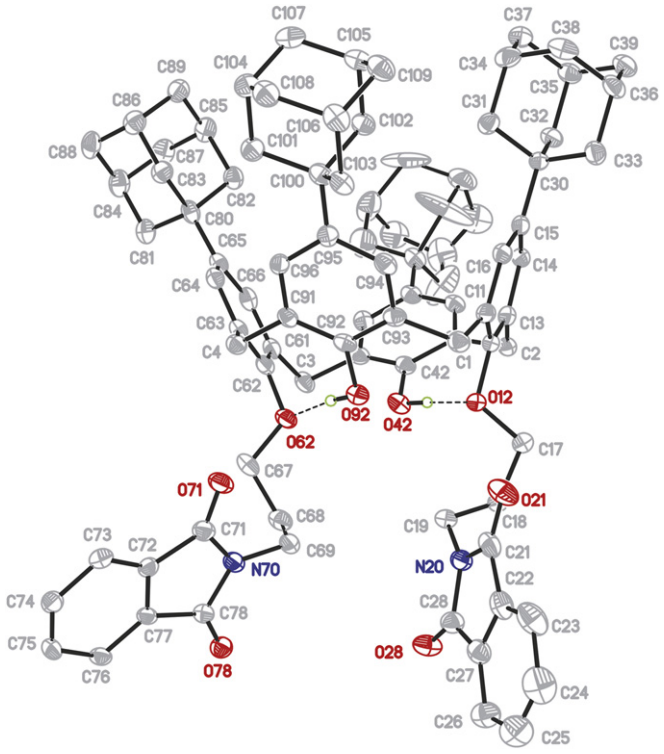


Fig. 1. Molecular structure of di-phthalimide **10**$_3$ (hydrogen atoms and solvent molecules are omitted).

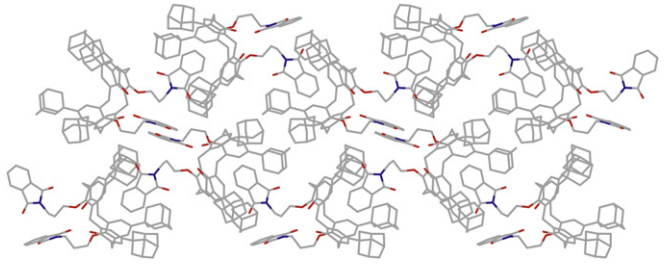


Fig. 2. Infinite chains formed by **10**$_3$ along *b*-axis by the phthalimide inclusion.

reacted with phthalimide under the Mitsunobu protocol to get the *cone* tetraphthalimide **14**$_2$ in high yield.

Cleavage of the phthalimide groups in **14**, **15** with hydrazine hydrate followed by acylation with *p*-nitrophenyl (diphenylphosphoryl) acetate led to target ligands bearing four equally attached CMPO-groups at the narrow rim (**7**), or two pairs of CMPO-groups connected to the calixarene phenolic oxygens by different linkers (**8**).

The di-phthalimide **10**$_2$ was used for the preparation of adamantylcalix[4]arenes with mixed functionalities at the narrow rim. The introduction of several different groups to a platform in a way when they create a common ligating environment can assist in fine tuning of the receptor molecule for a certain substrate. For these structural reasons ethyl 5-bromovalerate was chosen to introduce the ester/acid functionalities to the narrow rim of calixarene **10**$_2$. Despite the successful alkylation step (see Experimental section), the resultant di-phthalimide-di-ester **18** could not be selectively converted to di-acid or di-amine due to amidation of the ester groups with hydrazine hydrate or a partial hydrolysis of phthalimides when exposed to alkaline conditions. To overcome the difficulties, the di-phthalimide **10**$_2$ was converted to the trityl-protected di-amine **20** (Scheme 3, Trt=trityl=triphenylmethyl), which can be deprotected under acidic conditions. (The attempt to obtain calixarene **20** directly from **9** by the Mitsunobu alkylation with *N*-tritylethanolamine failed, probably due to the bulkiness of

Table 1
Crystal data and structure refinement details for **10**$_3$

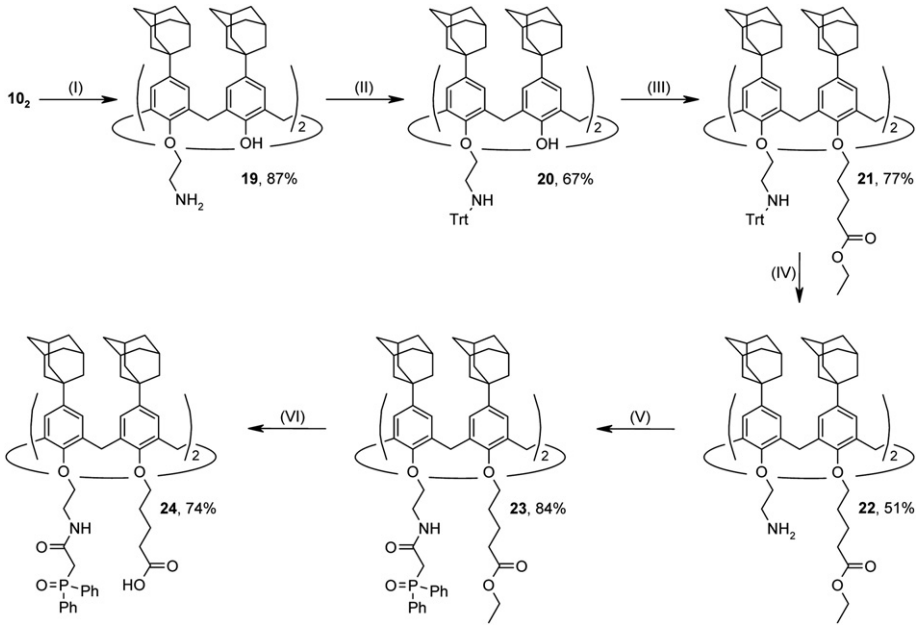
Empirical formula	$C_{90}H_{98}N_2O_8 \cdot CHCl_3$
Temperature	100 (2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/*c*
Z	8
Cell parameters	
a	33.395 (3) Å
b	23.6578 (16) Å
c	24.4989 (18) Å
α	90°
β	120.257 (5)°
γ	90°
Volume	16719 (2) Å^3
Density (calculated)	1.156 Mg/m^3
Absorption coefficient	0.165 mm^{-1}
F(000)	6192
Crystal size	0.42×0.36×0.22 mm^3
θ Range for data collection	1.97–26.07°
Index ranges	$-40\le h\le 41$, $-29\le k\le 29$, $-29\le l\le 30$
Reflections collected	62,830
Independent reflections	16,038 [*R*(int)=0.1032]
Completeness to *θ*=26.07°	96.7%
Absorption correction	Semi-empirical from equivalents
Max. and min transmission	0.9647 and 0.9341
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	16038/0/939
Goodness-of-fit on F^2	0.745
Final *R* indices [$I>2\sigma(I)$]	R_1=0.0640, wR_2=0.1286
R indices (all data)	R_1=0.1496, wR_2=0.1496
Largest diff. peak and hole	0.515 and −0.544 e Å^{-3}

reactants.) By the alkylation of **20** with ethyl 5-bromovalerate, calixarene **21** was obtained. In this molecule the amino or acid functionalities can be released independently by treatment with trifluoroacetic acid (TFA) or K_2CO_3, which were used for the high yield preparation of adamantylcalix[4]arenes with two CMPO and two ester (**23**) or acid (**24**) groups at narrow rim.

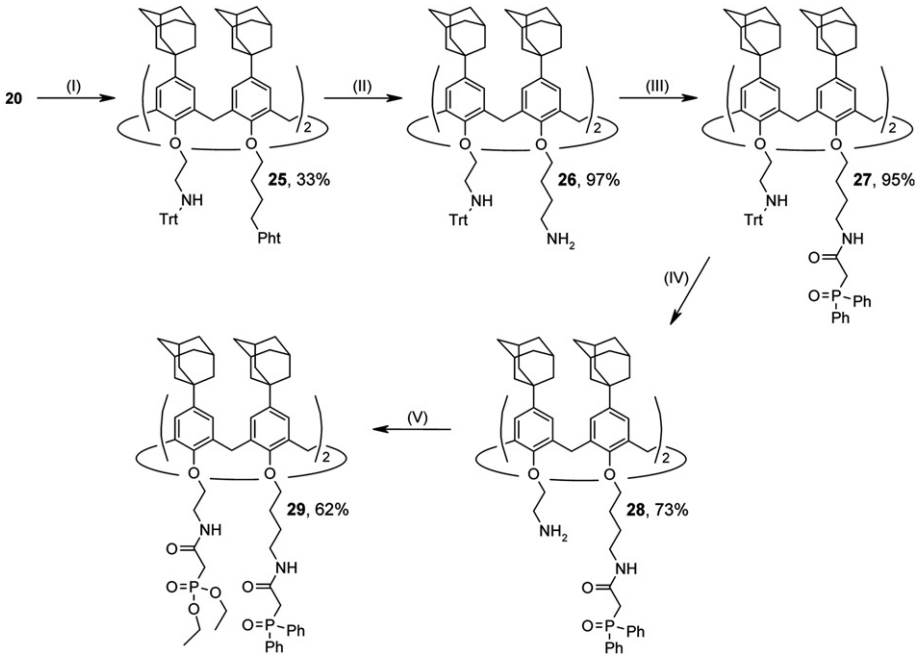
The trityl protection of amines at the narrow rim of calix[4] arenes can also be used for the introduction of two different amide groups to the molecule using the differences in the lability of trityl and phthalimide protecting groups. Thus, calixarene **20** was alkylated with 4-bromobutylphthalimide to give compound **25**, in which a pair of amino groups can be released selectively by hydrazine hydrate (Scheme 4). The sequential acylation with *p*-nitrophenyl (diphenylphosphoryl)acetate, deprotection of the remaining amino groups with TFA, and acylation with *p*-nitrophenyl (diethylphosphono)acetate, gave the adamantylcalixarene **29** bearing the two pairs of different CMPO-like ligating groups at the narrow rim in the alternating fashion.

2.2. Extraction studies

In the preliminary paper, the extraction of $^{241}Am^{3+}$ and $^{152}Eu^{3+}$ from 3 M HNO_3 solution into dichloromethane and *m*-nitro-trifluoromethylbenzene by CMPO-modified adamantylcalixarenes was studied and a high extraction ability of compounds **7**, **8** compared to 'monomeric' CMPOs (like **1**) was discovered.[15] Still, the influence of adamantane residues at the wide rim of calix[4]arene on the extraction ability of the narrow-rim tetra-CMPO derivatives, as well as the role of the CMPO-group attachment mode, remained unclear. Here, the extraction of the selected lanthanides and thorium by calixarene ligands **7** and **8** from 1 M HNO_3 solution into dichloromethane was studied spectrophotometrically using Arsenazo(III) to compare directly the extraction properties of the new ligands with those obtained earlier for ligands **3**–**5**.[10,20] The results are collected in Table 2 and compared in Fig. 3. As follows from Table 2, the best extractants for lanthanum, europium and



Scheme 3. Synthesis of calixarenes with mixed *O*-functionalities. (I) $N_2H_4 \cdot H_2O$, EtOH; (II) Ph_3CCl, Et_3N, CH_2Cl_2; (III) $Br(CH_2)_4CO_2Et$, NaH, DMF; (IV) TFA, CH_2Cl_2 then $NaHCO_3$; (V) *p*-nitrophenyl (diphenylphosphoryl)acetate, Et_3N, $CHCl_3$; (VI) K_2CO_3, H_2O/MeOH/THF.



Scheme 4. Synthesis of calixarenes with mixed amide functionalities. (I) $Br(CH_2)_4Pht$, NaH, DMF; (II) $N_2H_4 \cdot H_2O$, EtOH/THF; (III) *p*-nitrophenyl (diphenylphosphoryl)acetate, Et_3N, $CHCl_3$; (IV) TFA, CH_2Cl_2 then $NaHCO_3$; (V) *p*-nitrophenyl (diethylphosphono)acetate, Et_3N, $CHCl_3$.

thorium are CMPO-calixarenes **7_4** and **$8_{3/4}$**, in which four CMPO groups are connected to the calixarene core through flexible butylene or butylene/propylene linkers. The high thorium extraction level was also obtained for calixarene **7_3**. When moving towards more rigid ligands, the drastic decrease of lanthanide extraction appeared already with four propylene linkers between the calixarene platform and the CMPO groups, while the thorium extraction level remains the same. These data, including the small increase of the La^{3+} and Eu^{3+} extraction by **7_2** when compared to **7_3**, are in good agreement with known results for Ln/Th extraction by tetra-CMPO *tert*-butylcalix[4]arenes **3**.[10]

As follows from the extraction data for ligands **8**, which are of the novel type of *f*-element extractants as they have two pairs of CMPO groups of different flexibility at the narrow rim, the presence

Table 2
Distribution coefficients (D) for the extraction of lanthanides and thorium by CMPO/calixarenes **7** and **8**[a] from an aqueous phase ($c_M=10^{-4}$ M, 1 M HNO_3) into dichloromethane at 20 °C

Ligand	La^{3+}	Pr^{3+}	Nd^{3+}	Eu^{3+}	Yb^{3+}	Th^{4+}
7_2	0.54			0.49	0.20	2.57
7_3	0.30			0.28	0.22	5.67
7_4	4.88			4.26	1.17	5.67
$8_{2/3}$	0.43	0.52	0.43	0.25	0.49	2.23
$8_{2/4}$	0.43	0.59	0.47	0.41	0.49	2.33
$8_{3/4}$	4.26			4.26	0.41	4.56

[a] For all calixarenes $c_L=10^{-3}$ M for Ln^{3+} extraction and $c_L=10^{-4}$ M for Th^{4+} extraction.

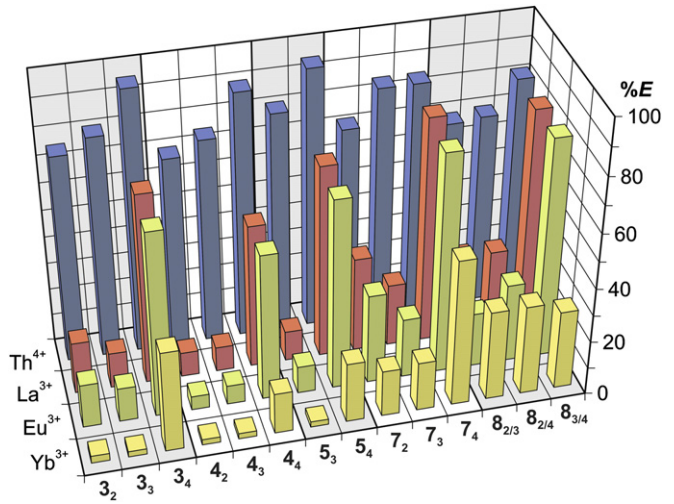


Fig. 3. The comparative plot for the extraction (%*E*) of lanthanides and thorium by CMPO/calixarenes **3**–**5**, **7** and **8** (see Table 2 for the experimental conditions). The data for **3** are from Ref. 10, the data for **4**, **5** are from Ref. 20.

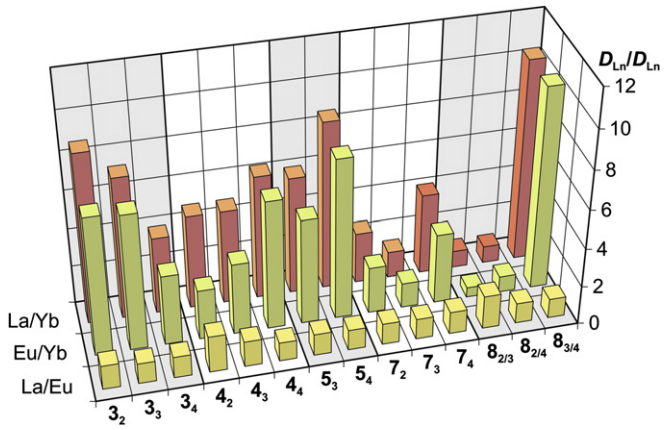


Fig. 4. The lanthanide/lanthanide selectivity for the extraction by CMPO/calixarenes **3**–**5**, **7** and **8**.

of two butylene- or propylene-linked CMPOs at the narrow rim of calix[4]arene is essential but insufficient to provide a high extraction towards lanthanides and thorium; the support of two other CMPO groups attached with the same rigidity and/or located within the same ligating environment is required. Thus, the ligands $\mathbf{8_{2/4}}$ and $\mathbf{8_{2/3}}$ are much less active as extractants if compared to $\mathbf{8_{3/4}}$; moreover, these ligands lose Ln/Ln and even Th/Ln selectivity.

The extraction data for the *p*-(1-adamantyl)calix[4]arene-based CMPO ligands can be directly compared with those for the *p*-*tert*-Bu (**3**), *p*-H (**4**) and *p*-*tert*-Oct (**5**) analogues. As follows from Fig. 3, the adamantylcalix[4]arenes surpass the former ligands for every type of linker between the CMPO groups and the calixarene platform in lanthanide extraction (e.g., $D_{Ln}(\mathbf{7_4})>D_{Ln}(\mathbf{3_4})>D_{Ln}(\mathbf{5_4})>D_{Ln}(\mathbf{4_4})$) but not thorium extraction. Among all of the CMPO ligands compared, the more Th/Ln selective are propylene-linked compounds, and the *p*-H-calixarene $\mathbf{5_3}$ is the most selective ($D_{Th}/D_{Ln}(\mathbf{5_3})>34$, $D_{Th}/D_{Ln}(\mathbf{4_3})>30$, $D_{Th}/D_{Ln}(\mathbf{3_3})>28$, $D_{Th}/D_{Ln}(\mathbf{7_3})>19$), although the *p*-H-calix[4]arene $\mathbf{4_2}$ with four ethylene-linked CMPO groups is also thorium selective ($D_{Th}/D_{Ln}(\mathbf{4_2})>24$).

The Ln/Ln selectivities expressed as D_{Ln}/D_{Ln} ratios for the ligands are presented in Fig. 4. Nearly no La/Eu selectivity was observed for all the ligands, while a La/Yb and Eu/Yb selectivity was achieved in some cases (e.g., $D_{La}(\mathbf{8_{3/4}})/D_{Yb}(\mathbf{8_{3/4}})=10.4$, $D_{La}(\mathbf{5_4})/D_{Yb}(\mathbf{5_4})=8.7$, $D_{La}(\mathbf{3_2})/D_{Yb}(\mathbf{3_2})=8.8$). (Still, this selectivity is significantly less than that of ligand **2** (Alk=C_5H_{11}) for which $D_{La}/D_{Yb}>1600$.[10]) In contrast to the extraction efficiency, no correlation with the wide rim substituent type can be found for the Ln/Ln selectivity. Most probably, a unique combination of the ligating cavity shape, its size, and the solvation of the complex extracted is responsible for the extraction selectivity in each case.

3. Conclusions

The series of calixarene-based narrow rim CMPO ligands was extended with the derivatives of *p*-(1-adamantyl)calix[4]arenes, including the previously unknown compounds with mixed functionalities. For the tetra-CMPO *p*-(1-adamantyl)calixarenes the extraction of selected lanthanides and thorium from acidic solutions into dichloromethane was studied, and the results compared with those for the analogous *p*-*tert*-Bu, *p*-H and *p*-*tert*-Oct-calixarenes. The adamantylcalixarenes were found to surpass the other calixarenes by the extraction efficiency towards lanthanum and europium, but possess lower Th/Ln selectivity. The synthetic approaches developed in this study may be used in 'general' calixarene chemistry for narrow rim modifications if derivatives with mixed amine or amide functionalities are required.

4. Experimental section

4.1. General

^{1}H, ^{13}C and ^{31}P NMR spectra were measured on Bruker Avance 400 and AC 300 spectrometers with solvent signals as internal reference (85% H_3PO_4 as external standard for ^{31}P NMR). Signals labelled with an asterisk * could not be attributed clearly without additional experiments. Signal attribution in ^{13}C spectra was assisted with APT and/or DEPT135 experiments. ESI and FD mass spectra were recorded on an Agilent 1100 LC/MS, Micromass Ultima 3 and Finnigan MAT 8230 instruments. Melting points are uncorrected.

4.2. Materials

Chemicals were commercial grade and used without further purification. Solvents were purified and dried according to standard procedures. *p*-(1-Adamantyl)calix[4]arene **9**,[21] tetrakis (ethoxycarbonylmethoxy)-*p*-(1-adamantyl)calix[4]arene **11**,[19] *p*-nitrophenyl (diphenylphosphoryl)acetate,[7] and *p*-nitrophenyl (diethylphosphono)acetate[22] were prepared according to the published procedures. Synthesis details (only the last step) and full spectral data for tetra-CMPO derivatives **7** and **8** were published earlier.[15]

4.2.1. Bis(2-N-phthalimidoethyl)calixarene $\mathbf{10_2}$. Under nitrogen, to a cooled (0 °C) solution of Ph_3P (9.44 g, 36 mmol) in dry THF (60 mL), diisopropylazodicarboxylate (DIAD) (7.08 mL, 36 mmol) was added dropwise at stirring. The suspension obtained was stirred for 30 min and then a suspension of calixarene **9** (1:1 *p*-xylene complex, 6.40 g, 6 mmol) and 2-hydroxyethylpthalimide (6.88 g, 36 mmol) in THF (200 mL) was added dropwise. The stirring was continued for 1 h at low temperature and then for 24 h at room temperature. The reaction mixture (clear solution) was concentrated in vacuo to an oil, which was triturated with methanol. The solid formed was separated, washed with methanol and dried. Yield 89% (6.98 g, white powder). Mp 234–236 °C (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (4H, m, ArH_{Pht}), 7.70 (4H, m, ArH_{Pht}), 6.96 (4H, s, ArH), 6.67 (4H, s, ArH), 6.65 (2H, s, OH), 4.44 (4H, t, J=6.6 Hz, NCH_2), 4.24 (4H, t, J=6.6 Hz, OCH_2), 4.18 (4H, d, J=2.9 Hz, $ArCH_2Ar$), 3.25 (4H, d, J=12.9 Hz, $ArCH_2Ar$), 2.10–1.35 (60H, m, H_{Ad}). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.10 (C=O), 150.47, 149.01, 146.87, 141.49 (C_{Ar}), 133.83 ($CH_{Ar,Pht}$), 132.13, 132.09 (C_{Ar}), 127.72

($C_{Ar,Pht}$), 124.96, 124.26 (CH_{Ar}), 123.22 ($CH_{Ar,Pht}$), 71.79 (OCH_2), 43.70, 42.74 (C_{Ad}), 37.47 (NCH_2), 36.91, 36.61 (C_{Ad}), 35.29, 35.26 (C_{Ad}), 31.11 ($ArCH_2Ar$), 29.08, 28.76 (CH_{Ad}). FD-MS: *m/z* 1308.5 $[M+H]^+$; $C_{88}H_{94}N_2O_8 \cdot H$ (1308.7).

4.2.2. Bis(3-N-phthalimidopropyl)calixarene ***10₃***. Under nitrogen, a mixture of calixarene **9** (2.13 g, 2.0 mmol) and K_2CO_3 (0.30 g, 2.2 mmol) in dry acetonitrile (150 mL) was stirred for 30 min. 3-Bromopropylphthalimide (1.10 g, 4.1 mmol) was added and the reaction mixture was stirred at reflux for 48 h. After cooling, the precipitate formed was separated, washed with acetonitrile, suspended in chloroform, filtered and filtrate evaporated. The remaining solid was re-crystallized from chloroform/methanol. Yield 72% (1.93 g, white powder). Mp >300 °C (decomp.). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (4H, m, ArH_{Pht}), 7.63 (4H, m, ArH_{Pht}), 7.24 (2H, s, OH), 7.02 (4H, s, ArH), 6.75 (4H, s, ArH), 4.29 (4H, d, *J*=12.8 Hz, $ArCH_2Ar$), 4.09 (8H, m, OCH_2, NCH_2), 3.31 (4H, d, *J*=2.8 Hz, $ArCH_2Ar$), 2.42 (4H, m, OCH_2CH_2), 2.08–1.82 (60H, m, H_{Ad}). FD-MS: *m/z* 1336.9 $[M+H]^+$; $C_{90}H_{98}N_2O_8 \cdot H$ (1336.8).

4.2.3. Bis(4-N-phthalimidobutyl)calixarene ***10₄***. Compound **10₄** was synthesized from calixarene **9** (2.13 g, 2.0 mmol), K_2CO_3 (0.30 g, 2.2 mmol) and 4-bromobutylphthalimide (1.16 g, 4.1 mmol) in dry acetonitrile (150 mL) as described for **10₃**. Yield 63% (1.70 g, white powder). Mp 190–192 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (4H, m, ArH_{Pht}), 7.64 (4H, m, ArH_{Pht}), 7.23 (2H, s, OH), 7.00 (4H, s, ArH), 6.73 (4H, s, ArH), 4.23 (4H, d, *J*=12.9 Hz, $ArCH_2Ar$), 4.01 (4H, t, *J*=5.9 Hz, NCH_2), 3.88 (4H, t, *J*=6.3 Hz, OCH_2), 3.27 (4H, d, *J*=12.9 Hz, $ArCH_2Ar$), 2.20–1.40 (68H, m, H_{Ad}+$OCH_2CH_2CH_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.41 (C=O), 150.72, 149.73, 146.83, 141.64 (C_{Ar}), 133.75 ($CH_{Ar,Pht}$), 132.55, 132.25 (C_{Ar}), 127.97 ($C_{Ar,Pht}$), 125.02 ($CH_{Ar,Pht}$), 124.49, 123.17 (CH_{Ar}), 75.67 (OCH_2), 43.81, 42.92 (C_{Ad}), 37.75 (NCH_2), 37.04, 36.77, 35.47, 35.40 (C_{Ad}), 31.56 ($ArCH_2Ar$), 29.22, 28.93 (CH_{Ad}), 27.32, 25.37 ($OCH_2CH_2CH_2$). ESI-MS: *m/z* 1402.8 $[M+K]^+$; $C_{92}H_{102}KN_2O_8$ (1402.9).

4.2.4. Tetrakis(2-hydroxyethyl)calixarene ***12***. A solution of calixarene **11** (1.04 g, 0.8 mmol) in dry THF (25 mL) was added dropwise to the stirred suspension of $LiAlH_4$ (0.61 g, 16 mmol) in dry THF (25 mL). The reaction mixture was stirred at reflux in dry atmosphere for 2 h. After cooling, water (0.61 mL), 3 M NaOH (0.61 mL) and second portion of water (1.83 mL) were added consecutively. The precipitate formed was filtered off and washed with THF. The filtrate was evaporated to dryness and the residue was triturated with methanol. Yield 81% (0.73 g, white powder). Mp 288–290 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 (8H, s, ArH), 5.11 (4H, br s, OH), 4.35 (4H, d, *J*=12.6 Hz, $ArCH_2Ar$), 4.01 (8H, br s, OCH_2), 3.97 (8H, br s, OCH_2), 3.24 (4H, d, *J*=12.6 Hz, $ArCH_2Ar$), 1.98 (12H, br s, CH_{Ad}), 1.80–1.55 (48H, m, $CH_{2,Ad}$). ^{13}C NMR (100 MHz, $CDCl_3$/CD_3OD) δ 151.72, 145.51, 133.26 (C_{Ar}), 124.75 (CH_{Ar}), 76.78 ($ArOCH_2$), 61.08 (CH_2OH), 43.11, 36.47, 35.16 (C_{Ad}), 29.88 ($ArCH_2Ar$), 28.69 (CH_{Ad}). ESI-MS: *m/z* 1160.0 $[M+Na]^+$; $C_{76}H_{96}NaO_8$ (1160.6).

4.2.5. Tetrakis(2-N-phthalimidoethyl)calixarene ***14₂***. Under nitrogen, to a cooled (0 °C) solution of Ph_3P (2.69 g, 10.2 mmol) in dry THF (20 mL), diethylazodicarboxylate (DEAD) (40% solution in toluene, 4.66 mL, 10.2 mmol) was added dropwise with stirring. After stirring for 30 min, phthalimide (1.51 g, 10.2 mmol) was added and stirring was continued for 15 min. A solution of calixarene **12** (0.73 g, 0.64 mmol) in dry THF (50 mL) was added dropwise and the resultant suspension was stirred at room temperature for 24 h. The reaction mixture (clear solution) was concentrated in vacuo to an oil, which was triturated with methanol. The solid formed was separated, washed with methanol and separated by column chromatography (gradient from chloroform to chloroform/ethanol, 20:1). Yield 83% (0.88 g, white powder). Mp 318–320 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (8H, m, ArH_{Pht}), 7.58 (8H, m, ArH_{Pht}), 6.76 (8H, s, ArH), 4.44 (4H, d, *J*=13.1 Hz, $ArCH_2Ar$), 4.41 (8H, t, *J*=7.2 Hz, OCH_2), 4.31 (8H, t, *J*=7.2 Hz, NCH_2), 3.20 (4H, d, *J*=13.1 Hz, $ArCH_2Ar$), 1.95 (12H, s, CH_{Ad}), 1.73–1.55 (48H, m, $CH_{2,Ad}$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.05 (C=O), 152.68, 144.92, 133.34 (C_{Ar}), 133.29 ($CH_{Ar,Pht}$), 132.32 ($C_{Ar,Pht}$), 124.62 (CH_{Ar}), 122.82 ($CH_{Ar,Pht}$), 70.48 (OCH_2), 43.26 (C_{Ad}), 38.09 (NCH_2), 36.81, 35.28 (C_{Ad}), 30.94 ($ArCH_2Ar$), 28.95 (CH_{Ad}). ESI-MS: *m/z* 1674.0 $[M+H_3O]^+$; $C_{108}H_{108}N_4O_{12} \cdot H_3O$ (1673.1).

4.2.6. Tris(3-N-phthalimidopropyl)calixarene ***13₃*** *and tetrakis(3-N-phthalimidopropyl)calixarene* ***14₃***. Under nitrogen, a mixture of calixarene **10₃** (1.11 g, 0.83 mmol) and NaH (100%, 0.06 g, 2.5 mmol) in dry DMF (50 mL) was stirred at room temperature for 30 min. 3-Bromopropylphthalimide (0.67 g, 2.5 mmol) was added and the mixture was stirred at 50 °C for 72 h. After cooling, several drops of water were added and the solvent was evaporated in vacuo. The residue was taken up in dichloromethane, washed with water and brine, dried over $MgSO_4$ and the solvent evaporated. The two major products were purified by flash chromatography (hexane/ethylacetate, gradient from 15:1 to 2:3) Compound. **13₃**: yield 35% (0.45 g, white powder). Mp >300 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (4H, m, ArH_{Pht}), 7.68 (4H, m, ArH_{Pht}), 7.63 (2H, m, ArH_{Pht}), 7.59 (2H, m, ArH_{Pht}), 7.08 (2H, s, ArH), 6.98 (2H, s, ArH), 6.57 (2H, d, *J*=2.3 Hz, ArH), 6.52 (2H, d, *J*=2.3 Hz, ArH), 5.68 (1H, s, OH), 4.35 (2H, d, *J*=12.5 Hz, $ArCH_2Ar$), 4.23 (2H, d, *J*=14.1 Hz, $ArCH_2Ar$), 4.04 (2H, t, *J*=8.2 Hz, OCH_2), 3.96–3.83 (10H, m, OCH_2+NCH_2), 3.24 (2H, d, *J*=14.1 Hz, $ArCH_2Ar$), 3.19 (2H, d, *J*=12.5 Hz, $ArCH_2Ar$), 2.70–2.50 (2H, m, OCH_2CH_2), 2.35–2.30 (4H, m, OCH_2CH_2), 2.08–1.38 (60H, m, H_{Ad}). FD-MS: *m/z* 1522.6 $[M]^+$; $C_{101}H_{107}N_3O_{10}$ (1522.9). Compound **14₃**: yield 34% (0.49 g, white powder). Mp 252–254 °C (decomp.). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (8H, m, ArH_{Pht}), 7.59 (8H, m, ArH_{Pht}), 6.98 (8H, s, ArH), 4.36 (4H, d, *J*=12.5 Hz, $ArCH_2Ar$), 3.98 (8H, t, *J*=7.5 Hz, OCH_2), 3.87 (8H, t, *J*=7.5 Hz, NCH_2), 3.13 (4H, d, *J*=12.5 Hz, $ArCH_2Ar$), 2.40 (8H, m, OCH_2CH_2), 2.04 (12H, m, CH_{Ad}), 1.72–1.58 (48H, m, $CH_{2,Ad}$). FD-MS: *m/z* 1711.2 $[M+H]^+$; $C_{112}H_{116}N_4O_{12} \cdot H$ (1711.2).

4.2.7. Tris(4-N-phthalimidobutyl)calixarene ***13₄*** *and tetrakis(4-N-phthalimidobutyl)calixarene* ***14₄***. Compounds **13₄** and **14₄** were obtained from calixarene **10₄** (0.68 g, 0.5 mmol), NaH (60% suspension, 0.08 g, 2.0 mmol) and 4-bromobutylphthalimide (0.56 g, 2.0 mmol) in dry DMF (20 mL) at room temperature for 72 h as described for **13₃** and **14₃**. The reaction mixture was quenched with 2 M HCl (50 mL), and the solid formed was collected by filtration, washed with water and dried. The two major products were purified by column chromatography (gradient from dichloromethane to dichloromethane/ethanol, 20:1). Compound **13₄**: yield 9% (0.07 g, white powder). Mp 166–168 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (4H, m, ArH_{Pht}), 7.73 (2H, m, ArH_{Pht}), 7.64 (4H, m, ArH_{Pht}), 7.58 (2H, m, ArH_{Pht}), 7.08 (2H, s, ArH), 6.95 (2H, s, ArH), 6.55 (2H, d, *J*=2.3 Hz, ArH), 6.48 (2H, d, *J*=2.3 Hz, ArH), 5.52 (1H, s, OH), 4.32 (2H, d, *J*=12.4 Hz, $ArCH_2Ar$), 4.13 (2H, d, *J*=12.9 Hz, $ArCH_2Ar$), 3.95 (2H, t, *J*=7.8 Hz, OCH_2), 3.90–3.74 (10H, m, OCH_2+NCH_2), 3.15 (4H, br d, $ArCH_2Ar$), 2.33 (2H, m, $OCH_2CH_2CH_2$), 2.10–1.35 (70H, m, $OCH_2CH_2CH_2$+$OCH_2CH_2CH_2$+H_{Ad}). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.27, 168.24 (C=O), 153.52, 151.29, 150.52, 145.80, 145.21, 141.58, 135.86 (C_{Ar}), 133.66, 133.42 ($CH_{Ar,Pht}$), 132.32, 132.22 ($C_{Ar,Pht}$), 132.03, 131.72, 129.12 (C_{Ar}), 125.11, 124.33, 124.27 (CH_{Ar}), 123.09, 122.93 ($CH_{Ar,Pht}$), 75.43, 73.78 (OCH_2), 43.80, 43.77, 42.88 (C_{Ad}), 38.13, 37.75 (NCH_2), 37.02, 37.00, 36.73 (C_{Ad}), 35.68, 35.34, 35.16 (C_{Ad}), 31.26, 30.95 ($ArCH_2Ar$), 29.20, 29.16, 28.88 (CH_{Ad}), 27.30, 27.19, 25.41, 25.21 ($OCH_2CH_2CH_2$). ESI-MS: *m/z* 1564.7 $[M]^+$; $C_{104}H_{113}N_3O_{10}$ (1565.1). Compound **14₄**: yield 17% (0.15 g, white powder). Mp 154–156 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (8H, m, ArH_{Pht}), 7.60 (8H, m, ArH_{Pht}), 6.78 (8H, s, ArH), 4.36 (4H, d,

J=12.3 Hz, $ArCH_2Ar$), 3.92 (8H, t, J=7.7 Hz, OCH_2)*, 3.77 (8H, t, J=7.5 Hz, NCH_2)*, 3.12 (4H, d, J=12.3 Hz, $ArCH_2Ar$), 2.10 (8H, m, $OCH_2CH_2CH_2$)*, 1.96 (12H, s, CH_{Ad}), 1.78 (8H, m, $OCH_2CH_2CH_2$)*, 1.75–1.55 (48H, m, $CH_{2,Ad}$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.13 (C=O), 153.24, 144.57, 133.79 (C_{Ar}), 133.54 ($CH_{Ar,Pht}$), 132.32 ($C_{Ar,Pht}$), 124.51 (CH_{Ar}), 123.01 ($CH_{Ar,Pht}$), 74.57 (OCH_2), 43.45 (C_{Ad}), 37.98 (NCH_2), 36.95, 35.40 (C_{Ad}), 30.96 ($ArCH_2Ar$), 29.11 (CH_{Ad}), 27.71, 25.40 ($OCH_2CH_2CH_2$). ESI-MS: m/z 1788.0 $[M+Na]^+$; $C_{116}H_{124}N_4NaO_{12}$ (1789.3).

4.2.8. Bis(2-N-phthalimidoethyl)-bis(3-N-phthalimidopropyl)calixarene ***15*****$_{2/3}$**. Compound **15$_{2/3}$** was obtained from calixarene **10$_2$** (0.59 g, 0.45 mmol), NaH (100%, 0.086 g, 3.6 mmol) and 3-bromopropylphthalimide (0.97 g, 3.6 mmol) in dry DMF (30 mL) at 60–65 °C for 100 h as described for **13$_3$** and **14$_3$**. After cooling, the reaction mixture was quenched with glacial acetic acid (2 mL) and water (30 mL). The solid formed was separated, washed with water and methanol, dissolved in chloroform. The chloroform solution was passed through thin layer of silica gel and then concentrated to almost dryness. The precipitate formed upon addition of hexane was collected by filtration, washed with hexane and dried. Yield 49% (0.37 g, white powder). Mp >300 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (8H, br s, ArH_{Pht}), 7.54 (4H, m, ArH_{Pht}), 7.42 (4H, m, ArH_{Pht}), 7.04 (4H, s, ArH), 6.57 (4H, s, ArH), 4.48 (4H, t, J=8.1 Hz, OCH_2CH_2N), 4.46 (4H, d, J=12.4 Hz, $ArCH_2Ar$), 4.31 (4H, t, J=8.1 Hz, OCH_2CH_2N), 4.08 (4H, t, J=6.8 Hz, $NCH_2CH_2CH_2$), 3.90 (4H, t, J=7.3 Hz, $OCH_2CH_2CH_2$), 3.22 (4H, d, J=12.4 Hz, $ArCH_2Ar$), 2.39 (4H, m, $OCH_2CH_2CH_2$), 2.09–1.39 (60H, m, H_{Ad}). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.07, 168.04 (C=O), 153.41, 152.16, 145.40, 144.22, 135.16 (C_{Ar}), 133.27, 132.98 ($CH_{Ar,Pht}$), 132.45 (C_{Ar}), 132.25, 132.04 ($C_{Ar,Pht}$), 124.93, 124.17 (CH_{Ar}), 122.80, 122.61 ($CH_{Ar,Pht}$), 73.26, 69.45 (OCH_2), 43.66, 42.95 (C_{Ad}), 37.92 (OCH_2CH_2N), 36.91, 36.72 (C_{Ad}), 35.78 ($NCH_2CH_2CH_2$), 35.53, 35.07 (C_{Ad}), 30.96 ($ArCH_2Ar$), 29.15 ($OCH_2CH_2CH_2$), 29.06, 28.86 (CH_{Ad}). FD-MS: m/z 1684.1 $[M+H]^+$; $C_{110}H_{112}N_4O_{12}\cdot H$ (1683.1).

4.2.9. Bis(2-N-phthalimidoethyl)-bis(4-N-phthalimidobutyl)calixarene ***15*****$_{2/4}$**. Compound **15$_{2/4}$** was obtained from calixarene **10$_2$** (0.59 g, 0.45 mmol), NaH (100%, 0.086 g, 3.6 mmol) and 4-bromobutylphthalimide (1.02 g, 3.6 mmol) in dry DMF (30 mL) at room temperature for 80 h as described for **15$_{2/3}$**. After passing through silica gel, the product was washed with methanol. Yield 38% (0.29 g, white powder). Mp >300 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (4H, m, ArH_{Pht}), 7.62–7.47 (12H, m, ArH_{Pht}), 7.07 (4H, s, ArH), 6.54 (4H, s, ArH), 4.48 (4H, t, J=8.0 Hz, OCH_2CH_2N), 4.42 (4H, d, J=12.6 Hz, $ArCH_2Ar$), 4.27 (4H, t, J=8.0 Hz, OCH_2CH_2N), 3.97 (4H, t, J=7.3 Hz, $NCH_2CH_2CH_2CH_2$), 3.67 (4H, t, J=7.3 Hz, $OCH_2CH_2CH_2CH_2$), 3.18 (4H, d, J=12.6 Hz, $ArCH_2Ar$), 2.15–1.42 (68H, m, $H_{Ad}+OCH_2CH_2CH_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.16 (br s, C=O), 153.78, 152.03, 145.45, 144.08, 135.41 (C_{Ar}), 133.43, 133.17 ($CH_{Ar,Pht}$), 132.42 (C_{Ar}), 132.08, 131.97 ($C_{Ar,Pht}$), 124.94, 124.05 (CH_{Ar}), 122.83, 122.75 ($CH_{Ar,Pht}$), 75.28, 69.61 (OCH_2), 43.74, 42.93 (C_{Ad}), 37.85, 37.76 (NCH_2), 36.94, 36.73, 35.59, 35.05 (C_{Ad}), 30.96 ($ArCH_2Ar$), 29.10, 28.87 (CH_{Ad}), 27.04, 25.23 ($OCH_2CH_2CH_2$). FD-MS: m/z 1712.6 $[M+H]^+$; $C_{112}H_{116}N_4O_{12}\cdot H$ (1711.2).

4.2.10. Bis(3-N-phthalimidopropyl)-bis(4-N-phthalimidobutyl)calixarene ***15*****$_{3/4}$**. Compound **15$_{3/4}$** was obtained from calixarene **10$_3$** (1.31 g, 0.98 mmol), NaH (100%, 0.072 g, 3.0 mmol) and 4-bromobutylphthalimide (0.85 g, 3.0 mmol) in dry DMF (50 mL) at room temperature for 72 h as described for **13$_3$** and **14$_3$**. The product was re-crystallized from dichloromethane/methanol (1:4). Yield 75% (1.27 g, white powder). Mp 182–183 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 7.77–7.70 (8H, m, ArH_{Pht}), 7.65–7.59 (8H, m, ArH_{Pht}), 6.96 (4H, s, ArH), 6.57 (4H, s, ArH), 4.33 (4H, d, J=12.5 Hz, $ArCH_2Ar$), 4.06 (4H, t, J=7.5 Hz, NCH_2), 3.85–3.76 (12H, m, NCH_2, OCH_2), 3.10 (4H, d, J=12.5 Hz, $ArCH_2Ar$), 2.53 (4H, m, $OCH_2CH_2CH_2$), 2.03–1.25 (68H, m, $H_{Ad}+OCH_2CH_2CH_2CH_2$). FD-MS: m/z 1738.5 $[M]^+$; $C_{114}H_{120}N_4O_{12}$ (1738.2).

4.2.11. Tetrakis(2-aminoethyl)calixarene ***16*****$_2$**. Hydrazine hydrate (2.4 mL, 50 mmol) was added to a stirred suspension of calixarene **14$_2$** (0.41 g, 0.25 mmol) in ethanol (20 mL) and THF (20 mL). The reaction mixture was refluxed overnight, cooled and concentrated under reduced pressure. Water was added and the product was extracted with chloroform, washed with water, and the solvent evaporated. Yield 89% (0.25 g, white powder). Mp 158–160 °C (decomp.). ^1H NMR (400 MHz, $CDCl_3$) δ 6.88 (8H, s, ArH), 4.32 (4H, d, J=12.4 Hz, $ArCH_2Ar$), 4.01 (8H, t, J=5.3 Hz, OCH_2), 3.28 (8H, t, J=5.3 Hz, NCH_2), 3.23 (4H, d, J=12.4 Hz, $ArCH_2Ar$), 1.97 (12H, s, CH_{Ad}), 1.75–1.55 (48H, m, $CH_{2,Ad}$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.80, 145.88, 133.52 (C_{Ar}), 124.96 (CH_{Ar}), 75.49 (OCH_2), 43.39 (C_{Ad}), 40.80 (NCH_2), 36.75, 35.46 (C_{Ad}), 30.35 ($ArCH_2Ar$), 28.93 (CH_{Ad}). ESI-MS: m/z 1157.6 $[M+Na]^+$; $C_{76}H_{100}N_4NaO_4$ (1156.6).

4.2.12. Tetrakis(3-aminopropyl)calixarene ***16*****$_3$**. Compound **16$_3$** was obtained from calixarene **14$_3$** (0.26 g, 0.15 mmol) and hydrazine hydrate solution (80%, 1.84 mL, 30 mmol) in ethanol (20 mL) as described for **16$_2$**. Yield 84% (0.15 g, white powder). Mp 262–264 °C (decomp.). ^1H NMR (300 MHz, $CDCl_3$) δ 6.85 (8H, s, ArH), 4.33 (4H, d, J=12.5 Hz, $ArCH_2Ar$), 3.95 (8H, t, J=6.8 Hz, OCH_2), 3.18 (4H, d, J=12.5 Hz, $ArCH_2Ar$), 3.05 (8H, m, NCH_2), 2.95 (8H, br s, NH_2), 2.19 (8H, m, OCH_2CH_2), 1.96 (12H, s, CH_{Ad}), 1.80–1.25 (48H, m, $CH_{2,Ad}$). FD-MS: m/z 1190.9 $[M+H]^+$; $C_{80}H_{108}N_4O_4\cdot H$ (1190.8).

4.2.13. Tetrakis(4-aminobutyl)calixarene ***16*****$_4$**. Compound **16$_4$** was obtained from calixarene **14$_4$** (0.15 g, 0.085 mmol) and hydrazine hydrate (0.5 mL, 10.2 mmol) in ethanol (20 mL) and THF (10 mL) as described for **16$_2$**. Yield 76% (0.08 g, white powder). Mp 192–194 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 6.79 (s, 8 H, ArH), 4.36 (4H, d, J=12.3 Hz, $ArCH_2Ar$), 3.85 (8H, t, J=7.6 Hz, OCH_2), 3.12 (4H, d, J=12.3 Hz, $ArCH_2Ar$), 2.77 (8H, m, NCH_2), 2.03 (8H, m, $OCH_2CH_2CH_2$)*, 1.96 (12H, s, CH_{Ad}), 1.80–1.56 (48H, m, $CH_{2,Ad}$), 1.54 (8H, m, $OCH_2CH_2CH_2$)*. ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.23, 144.57, 133.69 (C_{Ar}), 124.44 (CH_{Ar}), 75.01 (OCH_2), 43.40 (C_{Ad}), 42.37 (NCH_2), 36.86, 35.34 (C_{Ad}), 30.83 ($ArCH_2Ar$), 30.40 ($OCH_2CH_2CH_2$)*, 29.02 (CH_{Ad}), 27.72 ($OCH_2CH_2CH_2$)*. ESI-MS: m/z 1268.0 $[M+Na]^+$; $C_{84}H_{116}N_4NaO_4$ (1268.9).

4.2.14. Bis(2-aminoethyl)-bis(3-aminopropyl)calixarene ***17*****$_{2/3}$**. Compound **17$_{2/3}$** was obtained from calixarene **15$_{2/3}$** (0.34 g, 0.20 mmol) and hydrazine hydrate solution (80%, 4.9 mL, 80 mmol) in ethanol (20 mL) as described for **16$_2$**. The solid formed after addition of water was separated, washed with water and dried. Yield 86% (0.20 g, white powder). Mp 215–217 °C (decomp.). ^1H NMR (400 MHz, $CDCl_3$) δ 7.08 (4H, s, ArH), 6.60 (4H, s, ArH), 4.34 (4H, d, J=12.3 Hz, $ArCH_2Ar$), 4.02 (4H, t, J=5.2 Hz, OCH_2CH_2N), 3.83 (4H, t, J=7.5 Hz, $OCH_2CH_2CH_2$), 3.19 (4H, d, J=12.3 Hz, $ArCH_2Ar$), 3.18 (4H, t, J=5.2 Hz, OCH_2CH_2N), 2.84 (4H, t, J=7.0 Hz, $NCH_2CH_2CH_2$), 2.07 (12H, m, CH_{Ad}), 2.00 (4H, m, $OCH_2CH_2CH_2$), 1.93–1.42 (48H, m, $CH_{2,Ad}$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.65, 151.47, 145.29, 144.41, 134.98, 131.85 (C_{Ar}), 125.00, 124.21 (CH_{Ar}), 77.01, 73.85 (OCH_2), 43.65 (C_{Ad}), 43.44 (OCH_2CH_2N), 42.89 (C_{Ad}), 39.01 ($NCH_2CH_2CH_2$), 36.79, 36.58 (C_{Ad}), 35.47, 35.02 (C_{Ad}), 30.39 ($ArCH_2Ar$), 28.96 (CH_{Ad}), 28.88 ($OCH_2CH_2CH_2$), 28.74 (CH_{Ad}). FD-MS: m/z 1163.4 $[M+H]^+$; $C_{78}H_{104}N_4O_4\cdot H$ (1162.7).

4.2.15. Bis(2-aminoethyl)-bis(4-aminobutyl)calixarene ***17*****$_{2/4}$**. Compound **17$_{2/4}$** was obtained from calixarene **15$_{2/4}$** (0.29 g, 0.17 mmol) and hydrazine hydrate solution (80%, 4.1 mL, 68 mmol) in ethanol (15 mL) as described for **17$_{2/3}$**. Yield 94% (0.19 g, white powder). Mp 212–216 °C (decomp.). ^1H NMR (400 MHz, $CDCl_3$) δ 7.07 (4H, s,

ArH), 6.57 (4H, s, ArH), 4.32 (4H, d, J=12.3 Hz, $ArCH_2Ar$), 4.00 (4H, t, J=4.8 Hz, OCH_2CH_2N), 3.72 (4H, t, J=7.0 Hz, $OCH_2CH_2CH_2$), 3.15 (8H, m, $ArCH_2Ar$+NCH_2), 2.83–2.56 (12H, m, NCH_2+NH_2), 2.15–1.35 (68H, m, H_{Ad}+$OCH_2CH_2CH_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.64, 151.47, 145.26, 144.32, 135.04, 131.82 (C_{Ar}), 124.97, 124.15 (CH_{Ar}), 76.89, 75.91 (OCH_2), 43.65, 42.86 (C_{Ad}), 41.93, 41.78 (NCH_2), 36.79, 36.57 (C_{Ad}), 35.46, 35.00 (C_{Ad}), 30.37 ($ArCH_2Ar$), 29.80 ($OCH_2CH_2CH_2$)*, 28.95, 28.73 (CH_{Ad}), 27.25 ($OCH_2CH_2CH_2$)*. FD-MS: m/z 1191.6 $[M+H]^+$; $C_{80}H_{108}N_4O_4\cdot H$ (1190.8).

4.2.16. Bis(3-aminopropyl)-bis(4-aminobutyl)calixarene ***17*****$_{3/4}$**. Compound **17$_{3/4}$** was obtained from calixarene **15$_{3/4}$** (0.35 g, 0.20 mmol) and hydrazine hydrate solution (80%, 2.4 mL, 40 mmol) in ethanol (30 mL) as described for **16$_2$**. Yield 98% (0.24 g, white powder). Mp 272–274 °C (decomp.). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.92 (4H, s, ArH), 6.75 (4H, s, ArH), 4.34 (4H, d, J=12.5 Hz, $ArCH_2Ar$), 3.97 (4H, t, J=7.5 Hz, OCH_2), 3.85 (4H, t, J=7.5 Hz, OCH_2), 3.16 (4H, d, J=12.5 Hz, $ArCH_2Ar$), 3.15 (4H, m, NCH_2), 3.05 (4H, m, NCH_2), 2.84 (8H, br s, NH_2), 2.22 (4H, m, $OCH_2CH_2CH_2$), 2.03–1.25 (68H, m, H_{Ad}+$OCH_2CH_2CH_2CH_2CH_2$). FD-MS: m/z 1218.8 $[M+H]^+$; $C_{82}H_{112}N_4O_4\cdot H$ (1218.8).

4.2.17. Bis(2-N-phthalimidoethyl)-bis(4-ethoxycarbonylbutyl)calixarene ***18***. Compound **18** was obtained from calixarene **10$_2$** (0.59 g, 0.45 mmol), NaH (100%, 0.09 g, 3.6 mmol) and ethyl 5-bromovalerate (0.57 mL, 3.6 mmol) in dry DMF (30 mL) at 50–55 °C for 60 h as described for **13$_3$** and **14$_3$**. The reaction mixture was quenched with glacial acetic acid (2 mL) and then diluted with water (30 mL). The solid formed was filtered, washed with water and methanol, and dried. Yield 90% (0.63 g, white powder). Mp 166–168 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (8H, br s, ArH_{Pht}), 7.07 (4H, s, ArH), 6.55 (4H, s, ArH), 4.51 (4H, t, J=8.1 Hz, NCH_2), 4.43 (4H, d, J=12.5 Hz, $ArCH_2Ar$), 4.29 (4H, t, J=8.1 Hz, NCH_2CH_2), 3.97 (4H, q, J=7.2 Hz, OCH_2CH_3), 3.95 (4H, t, J=8.2 Hz, $OCH_2CH_2CH_2$), 3.19 (4H, d, J=12.5 Hz, $ArCH_2Ar$), 2.30 (4H, t, J=7.6 Hz, CH_2CO), 2.12–1.38 (68H, m, H_{Ad}+$OCH_2CH_2CH_2$), 1.13 (6H, t, J=7.2 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.51 (COO), 168.17 (CON), 153.70, 152.11, 145.51, 144.08, 135.31 (C_{Ar}), 133.33 ($CH_{Ar,Pht}$), 132.40 (C_{Ar}), 131.95 ($C_{Ar,Pht}$), 124.94, 124.04 (CH_{Ar}), 122.77 ($CH_{Ar,Pht}$), 75.48 ($OCH_2CH_2CH_2$), 69.58 (NCH_2CH_2), 59.85 (OCH_2CH_3), 43.71, 42.94 (C_{Ad}), 37.83 (NCH_2), 36.91, 36.71 (C_{Ad}), 35.56, 35.05 (C_{Ad}), 34.09 (CH_2CO), 30.96 ($ArCH_2Ar$), 29.26 ($OCH_2CH_2CH_2$)*, 29.07, 28.86 (CH_{Ad}), 21.61 ($OCH_2CH_2CH_2$)*, 14.08 (CH_3). FD-MS: m/z 1566.0 $[M+H]^+$; $C_{102}H_{118}N_2O_{12}\cdot H$ (1565.4).

4.2.18. Bis(2-aminoethyl)calixarene ***19***. Compound **19** was obtained from calixarene **10$_2$** (2.74 g, 2.1 mmol) and hydrazine hydrate solution (80%, 25.5 mL, 420 mmol) in ethanol (120 mL) as described for **16$_2$**. After cooling, water (20 mL) was added to the reaction mixture and the solid formed was separated, washed with cold ethanol and dried to give pure amine. Yield 87% (1.90 g, white powder). Mp 280–282 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (4H, s, ArH), 6.91 (4H, s, ArH), 4.30 (4H, d, J=12.9 Hz, $ArCH_2Ar$), 4.07 (4H, t, J=4.8 Hz, OCH_2), 3.36 (4H, d, J=12.9 Hz, $ArCH_2Ar$), 3.29 (4H, t, J=4.8 Hz, NCH_2), 2.06–1.50 (60H, m, H_{Ad}). FD-MS: m/z 1048.1 $[M+H]^+$; $C_{72}H_{90}N_2O_4\cdot H$ (1048.5).

4.2.19. Bis(2-tritylaminoethyl)calixarene ***20***. A solution of di-amine **19** (1.92 g, 1.84 mmol), triphenylchloromethane (1.23 g, 4.42 mmol) and triethylamine (0.62 mL, 4.42 mmol) in dry dichloromethane was stirred at room temperature for 2 h. The reaction mixture was washed with water, dried over $MgSO_4$ and concentrated in vacuo. The resultant oil was dissolved in minimal amount of acetone and the solution was heated to reflux and allowed to cool to room temperature. The crystalline solid formed was separated, washed with acetone and dried. Yield 67% (1.90 g, colourless needles). Mp 208–210 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (12H, m, ArH_{Trt}), 7.17 (12H, m, ArH_{Trt}), 7.10 (6H, m, ArH_{Trt}), 6.99 (4H, s, ArH), 6.65 (4H, s, ArH), 6.64 (2H, s, OH), 4.15 (4H, d, J=13.2 Hz, $ArCH_2Ar$), 3.97 (4H, t, J=4.7 Hz, OCH_2), 3.16 (4H, d, J=13.2 Hz, $ArCH_2Ar$), 2.62 (2H, br s, NH), 2.50 (4H, t, J=4.70 Hz, NCH_2), 2.12–1.38 (60H, m, H_{Ad}). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.48, 149.61, 146.63 (C_{Ar}), 146.02 ($C_{Ar,Trt}$), 141.48, 132.11 (C_{Ar}), 128.69 ($CH_{Ar,Trt}$), 127.73 (C_{Ar}), 127.66, 126.04 ($CH_{Ar,Trt}$), 124.91, 124.36 (CH_{Ar}), 76.10 (OCH_2), 70.66 (CPh_3), 43.71 (C_{Ad}), 43.44 (NCH_2), 42.77, 36.93, 36.63, 35.29 (C_{Ad}), 31.40 ($ArCH_2Ar$), 29.10, 28.78 (CH_{Ad}). FD-MS: m/z 1534.3 $[M+H]^+$; $C_{110}H_{118}N_2O_4\cdot H$ (1533.2).

4.2.20. Bis(2-tritylaminoethyl)-bis(4-ethoxycarbonylbutyl)calixarene ***21***. Compound **21** was obtained from calixarene **20** (1.92 g, 1.25 mmol), NaH (100%, 0.24 g, 10.0 mmol) and ethyl 5-bromovalerate (1.58 mL, 10.0 mmol) in dry DMF (180 mL) at room temperature for 36 h as described for **13$_3$** and **14$_3$**. After quenching, the reaction mixture was extracted with chloroform, washed with water, dried over $MgSO_4$, and the solvent evaporated. The solid formed upon addition of acetone was collected, washed with acetone and dried. Yield 77% (1.73 g, white powder). Mp 206–208 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (12H, m, ArH_{Trt}), 7.27 (12H, t, ArH_{Trt}), 7.16 (6H, m, ArH_{Trt}), 6.86 (4H, s, ArH), 6.65 (4H, s, ArH), 4.20 (4H, d, J=12.4 Hz, $ArCH_2Ar$), 4.13 (4H, q, J=7.2 Hz, OCH_2CH_3), 4.05 (4H, t, J=5.1 Hz, OCH_2CH_2N), 3.66 (4H, t, J=7.7 Hz, $OCH_2CH_2CH_2$), 3.01 (4H, d, J=12.4 Hz, $ArCH_2Ar$), 2.58 (4H, t, J=5.1 Hz, NCH_2), 2.16 (4H, t, J=7.7 Hz, CH_2CO), 2.15–1.50 (68H, m, H_{Ad}+$OCH_2CH_2CH_2$), 1.27 (6H, t, J=7.2 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.24 (C=O), 153.41, 152.55 (C_{Ar}), 145.98 ($C_{Ar,Trt}$), 144.66, 144.31, 134.18, 132.77 (C_{Ar}), 128.45, 127.65, 126.07 ($CH_{Ar,Trt}$), 124.47, 124.23 (CH_{Ar}), 74.86, 74.11 (OCH_2), 70.53 (CPh_3), 60.03 (OCH_2CH_3), 44.12 (NCH_2), 43.45, 43.13 (C_{Ad}), 36.83, 36.75 (C_{Ad}), 35.34, 35.12 (C_{Ad}), 34.16 (CH_2CO), 30.95 ($ArCH_2Ar$), 29.39 ($OCH_2CH_2CH_2$)*, 28.99, 28.90 (CH_{Ad}), 21.27 ($OCH_2CH_2CH_2$)*, 14.20 (CH_3). FD-MS: m/z 1789.8 $[M+H]^+$; $C_{124}H_{142}N_2O_8\cdot H$ (1789.5).

4.2.21. Bis(2-aminoethyl)-bis(4-ethoxycarbonylbutyl)calixarene ***22***. TFA (10 mL) was added dropwise to the stirred solution of calixarene **21** (1.61 g, 0.9 mmol) in dichloromethane (20 mL). After stirring for 2 h at room temperature, the reaction mixture was concentrated in vacuo. The rest was taken up in chloroform, washed with 1 M $NaHCO_3$, water and dried over $MgSO_4$. The solid formed after evaporation of the solvent was washed with diethyl ether and dried. Yield 51% (0.60 g, white powder). Mp 280–282 °C (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (4H, s, ArH), 6.57 (4H, s, ArH), 4.28–4.16 (8H, m, $ArCH_2Ar$+OCH_2CH_2N), 4.08 (4H, q, J=7.2 Hz, OCH_2CH_3), 3.92 (4H, t, J=7.5 Hz, $OCH_2CH_2CH_2$), 3.43 (4H, t, J=4.1 Hz, NCH_2), 3.23 (4H, d, J=12.6 Hz, $ArCH_2Ar$), 2.38 (4H, t, J=7.3 Hz, CH_2CO), 2.15–1.38 (68H, m, H_{Ad}+$OCH_2CH_2CH_2$), 1.20 (6H, t, J=7.2 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.48 (C=O), 153.21, 150.11, 146.40, 145.23, 134.68, 131.63 (C_{Ar}), 125.34, 124.59 (CH_{Ar}), 76.31, 72.53 (OCH_2), 60.21 (OCH_2CH_3), 43.70, 42.84 (C_{Ad}), 39.91 (NCH_2), 36.78, 36.55 (C_{Ad}), 35.61, 35.10 (C_{Ad}), 33.78 (CH_2CO), 30.62 ($ArCH_2Ar$), 28.95 (CH_{Ad}), 28.85 ($OCH_2CH_2CH_2$)*, 28.71 (CH_{Ad}), 21.25 ($OCH_2CH_2CH_2$)*, 14.09 (CH_3). FD-MS: m/z 1305.5 $[M+H]^+$; $C_{86}H_{114}N_2O_8\cdot H$ (1304.9).

4.2.22. Bis[2-(diphenylphosphorylacetylamino)ethyl]-bis(4-ethoxycarbonylbutyl)calixarene ***23***. A mixture of calixarene **22** (0.60 g, 0.46 mmol), *p*-nitrophenyl (diphenylphosphoryl)acetate (0.44 g, 1.15 mmol) and triethylamine (0.26 mL, 1.84 mmol) in chloroform (60 mL) was stirred at room temperature for 10 h. The solution was washed repeatedly with 1 M Na_2CO_3 and subsequently with water, dried over $MgSO_4$, and the solvent evaporated. The remaining solid was washed with diethyl ether and dried. Yield 84% (0.69 g, beige powder). Mp 161–163 °C. ^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.85–7.75 (8H, m, ArH_{Ph}), 7.55–7.40 (12H, m, ArH_{Ph}), 7.03 (4H, s, ArH), 6.49 (4H, s, ArH), 4.23 (4H, d, *J*=12.3 Hz, $ArCH_2Ar$), 4.05 (4H, q, *J*=7.2 Hz, OCH_2CH_3), 3.96 (4H, t, *J*=5.9 Hz, OCH_2CH_2N)*, 3.90 (4H, t, *J*=5.9 Hz, NCH_2)*, 3.69 (4H, t, *J*=7.0 Hz, $OCH_2CH_2CH_2$), 3.45 (4H, d, *J*=14.0 Hz, PCH_2), 3.12 (4H, d, *J*=12.3 Hz, $ArCH_2Ar$), 2.27 (4H, t, *J*=7.3 Hz, CH_2CO), 2.10–1.38 (68H, m, H_{Ad}+$OCH_2CH_2CH_2$), 1.19 (6H, t, *J*=7.2 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.54 (C=O), 164.94 (d, *J*=4.3 Hz, C=O), 153.59, 151.82, 145.25, 144.15, 134.92 (C_{Ar}), 132.18 (d, *J*=103.4 Hz, $C_{Ar,Ph}$), 131.82 (d, *J*=2.2 Hz, $CH_{Ar,Ph}$), 131.63 (C_{Ar}), 130.86 (d, *J*=9.8 Hz, $CH_{Ar,Ph}$), 128.40 (d, *J*=12.3 Hz, $CH_{Ar,Ph}$), 125.86, 123.92 (CH_{Ar}), 75.21, 71.53 (OCH_2), 60.05 (OCH_2CH_3), 43.59, 42.80 (C_{Ad}), 39.71 (NCH_2), 39.19 (d, *J*=62.1 Hz, PCH_2), 36.80, 36.59 (C_{Ad}), 35.43, 34.94 (C_{Ad}), 33.89 (CH_2CO), 30.73 ($ArCH_2Ar$), 29.23 ($OCH_2CH_2CH_2$)*, 28.96, 28.74 (CH_{Ad}), 21.54 ($OCH_2CH_2CH_2$)*, 14.05 (CH_3). ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.47 (P=O). ESI-MS: *m*/*z* 1810.92 $[M+Na]^+$; $C_{114}H_{136}N_2NaO_{12}P_2$ (1811.28).

4.2.23. Bis[2-(diphenylphosphorylacetylamino)ethyl]-bis(4-carboxybutyl)calixarene ***24***. A mixture of ester **23** (0.57 g, 0.32 mmol), K_2CO_3 (0.44 g, 3.19 mmol), water (4 mL), THF (10 mL) and methanol (40 mL) was stirred at reflux for 3 h. The reaction mixture was concentrated in vacuo and triturated with 2 M HCl (25 mL). The solid formed was separated, washed with water, dried and re-precipitated from chloroform upon addition of hexane. Yield 74% (0.41 g, white powder). Mp 202–204 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78–7.72 (8H, m, ArH_{Ph}), 7.55–7.42 (12H, m, ArH_{Ph}), 6.94 (4H, s, ArH), 6.57 (4H, s, ArH), 4.28 (4H, d, *J*=12.3 Hz, $ArCH_2Ar$), 4.03 (4H, t, *J*=7.5 Hz, OCH_2CH_2N)*, 3.86 (4H, m, NCH_2)*, 3.71 (4H, t, *J*=6.5 Hz, $OCH_2CH_2CH_2$), 3.54 (4H, d, *J*=13.6 Hz, PCH_2), 3.11 (4H, d, *J*=12.3 Hz, $ArCH_2Ar$), 2.36 (4H, t, *J*=6.5 Hz, CH_2CO), 2.08–1.42 (68H, m, H_{Ad}+$OCH_2CH_2CH_2$). ^{13}C NMR (100 MHz, $CDCl_3$/CD_3OD) δ 176.69 (C=O), 164.81 (d, *J*=4.9 Hz, C=O), 153.24, 152.08, 145.20, 144.24, 134.61 (C_{Ar}), 132.27 (d, *J*=2.2 Hz, $CH_{Ar,Ph}$), 130.79 (d, *J*=9.8 Hz, $CH_{Ar,Ph}$), 130.48 (d, *J*=104.6 Hz, $C_{Ar,Ph}$), 128.50 (d, *J*=12.3 Hz, $CH_{Ar,Ph}$), 131.85 (C_{Ar}), 124.72, 123.95 (CH_{Ar}), 75.15, 70.94 (OCH_2), 43.46, 42.81 (C_{Ad}), 39.60 (NCH_2), 38.91 (d, *J*=61.5 Hz, PCH_2), 36.68, 36.51 (C_{Ad}), 35.32, 34.93 (C_{Ad}), 33.79 (CH_2CO), 30.48 ($ArCH_2Ar$), 29.45 ($OCH_2CH_2CH_2$)*, 28.87, 28.69 (CH_{Ad}), 21.96 ($OCH_2CH_2CH_2$)*. ^{31}P NMR (162 MHz, $CDCl_3$/CD_3OD) δ 37.05 (P=O). ESI-MS: *m*/*z* 1754.99 $[M+Na]^+$; $C_{110}H_{128}N_2NaO_{12}P_2$ (1755.17).

4.2.24. Bis(2-tritylaminoethyl)-bis(4-N-phthalimidobutyl)calixarene ***25***. Compound **25** was obtained from calixarene **20** (1.84 g, 1.2 mmol), NaH (100%, 0.23 g, 9.6 mmol) and 4-bromobutylphthalimide (2.71 g, 9.6 mmol) in dry DMF (120 mL) at room temperature for 36 h as described for $\mathbf{13_3}$ and $\mathbf{14_3}$. The product was purified by column chromatography (gradient from chloroform to chloroform/ethanol, 20:1). Yield 33% (0.76 g, white powder). Mp 198–200 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (4H, m, ArH_{Pht}), 7.65 (4H, m, ArH_{Pht}), 7.36 (12H, m, ArH_{Trt}), 7.19 (12H, m, ArH_{Trt}), 7.07 (6H, m, ArH_{Trt}), 6.80 (4H, s, ArH), 6.62 (4H, s, ArH), 4.17 (4H, d, *J*=12.4 Hz, $ArCH_2Ar$), 4.08 (4H, t, *J*=5.8 Hz, OCH_2CH_2N), 3.68 (4H, t, *J*=7.3 Hz, $OCH_2CH_2CH_2$), 3.54 (4H, t, *J*=7.5 Hz, $NCH_2CH_2CH_2$), 2.96 (4H, d, *J*=12.4 Hz, $ArCH_2Ar$), 2.53 (4H, br s, NCH_2CH_2O), 2.10–1.45 (68H, m, H_{Ad}+$OCH_2CH_2CH_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.04 (C=O), 153.40, 152.69 (C_{Ar}), 146.01 ($C_{Ar,Trt}$), 144.63, 144.31, 134.10 (C_{Ar}), 133.65 ($CH_{Ar,Pht}$), 132.91 (C_{Ar}), 132.19 ($C_{Ar,Pht}$), 128.50, 127.63, 126.01 ($CH_{Ar,Trt}$), 124.48, 124.28 (CH_{Ar}), 122.99 ($CH_{Ar,Pht}$), 74.81, 73.99 (OCH_2), 70.62 (CPh_3), 44.26 (NCH_2CH_2O), 43.43, 43.16 (C_{Ad}), 37.87 ($NCH_2CH_2CH_2$), 36.87, 36.80 (C_{Ad}), 35.35, 35.15 (C_{Ad}), 31.09 ($ArCH_2Ar$), 29.02, 28.94 (CH_{Ad}), 27.34, 25.15 ($OCH_2CH_2CH_2$). FD-MS: *m*/*z* 1936.0 $[M+H]^+$; $C_{134}H_{140}N_4O_8$·H (1935.6).

4.2.25. Bis(2-tritylaminoethyl)-bis(4-aminobutyl)calixarene ***26***. Compound **26** was obtained from calixarene **25** (0.63 g, 0.33 mmol) and hydrazine hydrate solution (80%, 1.6 mL, 26.1 mmol) in ethanol (50 mL) and THF (50 mL) as described for $\mathbf{16_2}$. Yield 97% (0.53 g, white powder). Mp 195–197 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (12H, m, ArH_{Trt}), 7.25 (12H, m, ArH_{Trt}), 7.16 (6H, m, ArH_{Trt}), 6.89 (4H, s, ArH), 6.59 (4H, s, ArH), 4.20 (4H, d, *J*=12.3 Hz, $ArCH_2Ar$), 4.00 (4H, t, *J*=5.9 Hz, OCH_2CH_2N), 3.69 (4H, t, *J*=7.8 Hz, $OCH_2CH_2CH_2$), 2.99 (4H, d, *J*=12.3 Hz, $ArCH_2Ar$), 2.57 (4H, t, *J*=5.9 Hz, NCH_2CH_2O), 2.54 (4H, t, *J*=7.7 Hz, CH_2NH_2), 2.10–1.45 (68H, m, H_{Ad}+$OCH_2CH_2CH_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.63, 152.50 (C_{Ar}), 146.01 ($C_{Ar,Trt}$), 144.76, 144.30, 134.48, 132.51 (C_{Ar}), 128.49, 127.70, 126.12 ($CH_{Ar,Trt}$), 124.58, 124.20 (CH_{Ar}), 75.13, 74.43 (OCH_2), 70.71 (CPh_3), 44.07 (NCH_2CH_2O), 43.54, 43.10 (C_{Ad}), 42.15 (CH_2NH_2), 36.88, 36.75 (C_{Ad}), 35.42, 35.12 (C_{Ad}), 30.97 ($ArCH_2Ar$), 30.22 ($OCH_2CH_2CH_2$)*, 29.03, 28.90 (CH_{Ad}), 27.34 ($OCH_2CH_2CH_2$)*. FD-MS: *m*/*z* 1677.0 $[M+H]^+$; $C_{118}H_{136}N_4O_4$·H (1675.4).

4.2.26. Bis(2-tritylaminoethyl)-bis[4-(diphenylphosphorylacetylamino)butyl]calixarene ***27***. Compound **27** was obtained from calixarene **26** (0.53 g, 0.32 mmol), *p*-nitrophenyl (diphenylphosphoryl)acetate (0.30 g, 0.79 mmol) and triethylamine (0.18 mL, 1.27 mmol) in chloroform (60 mL) as described for **23**. The product was purified by re-precipitation from chloroform upon addition of hexane. Yield 95% (0.65 g, beige powder). Mp 165–167 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78–7.72 (8H, m, ArH_{Ph}), 7.53–7.39 (12H, m, ArH_{Ph}), 7.36 (12H, m, ArH_{Trt}), 7.20 (12H, m, ArH_{Trt}), 7.10 (6H, m, ArH_{Trt}), 6.80 (4H, s, ArH), 6.63 (4H, s, ArH), 4.16 (4H, d, *J*=12.4 Hz, $ArCH_2Ar$), 4.05 (4H, t, *J*=5.8 Hz, OCH_2CH_2N), 3.56 (4H, t, *J*=7.5 Hz, $OCH_2CH_2CH_2$), 3.32 (4H, d, *J*=12.9 Hz, PCH_2), 3.01 (4H, m, $NCH_2CH_2CH_2$), 2.95 (4H, d, *J*=12.4 Hz, $ArCH_2Ar$), 2.53 (4H, br s, NCH_2CH_2O), 2.03–1.52 (68H, m, H_{Ad}+$OCH_2CH_2CH_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.43 (d, *J*=4.3 Hz, C=O), 153.40, 152.60 (C_{Ar}), 145.98 ($C_{Ar,Trt}$), 144.54, 144.29, 133.96, 132.91 (C_{Ar}), 132.15 (d, *J*=2.5 Hz, $CH_{Ar,Ph}$), 131.72 (d, *J*=102.8 Hz, $C_{Ar,Ph}$), 130.39 (d, *J*=9.8 Hz, $CH_{Ar,Ph}$), 128.70 (d, *J*=12.3 Hz. $CH_{Ar,Ph}$), 128.45, 127.64, 126.05 ($CH_{Ar,Trt}$), 124.41, 124.25 (CH_{Ar}), 74.65, 74.12 (OCH_2), 70.58 (CPh_3), 44.19 (NCH_2CH_2O), 43.40, 43.15 (C_{Ad}), 39.95 ($NCH_2CH_2CH_2$), 38.62 (d, *J*=60.3 Hz, PCH_2), 36.83, 36.77 (C_{Ad}), 35.31, 35.13 (C_{Ad}), 31.04 ($ArCH_2Ar$), 28.98, 28.92 (CH_{Ad}), 27.39, 25.76 ($OCH_2CH_2CH_2$). ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.74 (P=O). ESI-MS: *m*/*z* 2159.28 $[M]^+$; $C_{146}H_{158}N_4O_8P_2$ (2158.83).

4.2.27. Bis(2-aminoethyl)-bis[4-(diphenylphosphorylacetylamino)butyl]calixarene ***28***. Compound **28** was obtained from calixarene **27** (0.65 g, 0.30 mmol) and TFA (10 mL) in dichloromethane (20 mL) as described for **22**. Yield 73% (0.37 g, beige powder). Mp 207–209 °C (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (2H, m, NH), 7.78–7.68 (8H, m, ArH_{Ph}), 7.55–7.36 (12H, m, ArH_{Ph}), 7.13 (4H, s, ArH), 6.57 (4H, s, ArH), 4.26 (4H, d, *J*=12.4 Hz, $ArCH_2Ar$), 4.09 (4H, t, *J*=4.5 Hz, OCH_2CH_2N), 3.69 (4H, t, *J*=7.3 Hz, $OCH_2CH_2CH_2$), 3.42 (4H, d, *J*=13.3 Hz, PCH_2), 3.30 (4H, t, *J*=4.5 Hz, NCH_2CH_2O), 3.26 (4H, m, $NCH_2CH_2CH_2$), 3.20 (4H, d, *J*=12.4 Hz, $ArCH_2Ar$), 2.15–1.35 (68H, m, H_{Ad}+$OCH_2CH_2CH_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.56 (d, *J*=4.9 Hz, C=O), 153.26, 150.78, 146.00, 144.92, 135.02 (C_{Ar}), 132.10 (d, *J*=2.5 Hz, $CH_{Ar,Ph}$), 131.59 (C_{Ar}), 131.51 (d, *J*=104.0 Hz, $C_{Ar,Ph}$), 130.73 (d, *J*=9.8 Hz, $CH_{Ar,Ph}$), 128.60 (d, *J*=11.7 Hz, $CH_{Ar,Ph}$), 125.29, 124.39 (CH_{Ar}), 76.31, 74.31 (OCH_2), 43.72, 42.86 (C_{Ad}), 40.71, 39.14 (NCH_2), 38.77 (d, *J*=59.1 Hz, PCH_2), 36.81, 36.58 (C_{Ad}), 35.59, 35.08 (C_{Ad}), 30.39 ($ArCH_2Ar$), 28.98, 28.73 (CH_{Ad}), 27.03, 25.43 ($OCH_2CH_2CH_2$). ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.80 (P=O). ESI-MS: *m*/*z* 1674.96 $[M]^+$; $C_{108}H_{130}N_4O_8P_2$ (1674.19).

4.2.28. Bis[2-(diethoxyphosphorylacetylamino)ethyl]-bis[4-(diphenylphosphorylacetylamino)butyl]calixarene ***29***. Compound **29** was obtained from calixarene **28** (0.37 g, 0.22 mmol), *p*-nitrophenyl (diethylphosphono)acetate (0.35 g, 1.11 mmol) and triethylamine (0.25 mL, 1.77 mmol) in chloroform (20 mL) as described for **23**. Yield 62% (0.28 g, beige powder). Mp 169–171 °C. ^{1}H NMR

(400 MHz, $CDCl_3$) δ 8.31 (2H, m, NH), 7.97 (2H, m, NH), 7.78–7.68 (8H, m, ArH_{Ph}), 7.50–7.35 (12H, m, ArH_{Ph}), 7.08 (4H, s, ArH), 6.48 (4H, s, ArH), 4.24 (4H, d, J=12.4 Hz, $ArCH_2Ar$), 4.15–4.00 (16H, m, OCH_2CH_3+OCH_2), 3.58 (4H, t, J=6.6 Hz, NCH_2), 3.39 (4H, d, J=14.0 Hz, CH_2PPh), 3.23 (4H, m, NCH_2), 3.10 (4H, d, J=12.4 Hz, $ArCH_2Ar$), 3.03 (4H, d, J=21.5 Hz, CH_2POCH_2), 2.15–1.35 (68H, m, H_{Ad}+$OCH_2CH_2CH_2$), 1.27 (12H, t, J=7.2 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.74 (d, J=5.5 Hz, C=O), 164.28 (d, J=4.9 Hz, C=O), 153.89, 151.78, 145.39, 144.14, 135.24 (C_{Ar}), 132.02 (d, J=2.4 Hz, $CH_{Ar,Ph}$), 131.51 (C_{Ar}), 131.47 (d, J=103.4 Hz, $C_{Ar,Ph}$), 130.66 (d, J=9.8 Hz, $CH_{Ar,Ph}$), 128.50 (d, J=12.3 Hz, $CH_{Ar,Ph}$), 124.92, 123.94 (CH_{Ar}), 75.59, 71.48 (OCH_2), 62.29 (d, J=6.2 Hz, OCH_2CH_3), 43.71, 42.78 (C_{Ad}), 39.87, 39.62 (NCH_2), 39.27 (d, J=61.5 Hz, CH_2PPh), 36.83, 36.59, 35.51 (C_{Ad}), 35.09 (d, J=133.5 Hz, CH_2POCH_2), 34.94 (C_{Ad}), 30.54 ($ArCH_2Ar$), 28.99, 28.74 (CH_{Ad}), 27.42, 25.96 ($OCH_2CH_2CH_2$), 16.20 (d, J=6.2, CH_3). ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.03, 23.67 (P=O). FD-MS: m/z 2054.3 $[M+Na]^+$; $C_{120}H_{152}N_4NaO_{16}P_4$ (2053.4).

4.3. Extraction of lanthanide and thorium nitrates into dichloromethane

The aqueous phase consisted of a solution of lanthanide or thorium nitrate and HNO_3, in bi-distilled water; the organic phase was a solution of the ligand in dichloromethane, at a concentration, suited for an extraction percentage ranging between 10 and 90%. A 1 mL aliquot of each phase was stirred in a stoppered tube immersed in a thermostated bath at 20 °C for 12 h. After separation of the two phases, the concentration of the cation remaining in the aqueous phase was monitored spectrophotometrically using Arsenazo(III) (3,6-bis(*o*-arsonophenyl)-4,5-dihydroxy-2,7-naphthalenedisulfonic acid) as reagent. The Arsenazo solution (5 mL, c=6.4×10^{-4} M) was added to a 0.65 mL aliquot of the aqueous phase. The volume of this sample was then adjusted to 50 mL with a sodium formiate-formic acid buffer (pH 2.8) for the determination of lanthanides and with HNO_3 (4 M) for the determination of thorium. The absorbances (A) were measured at 665 nm for thorium and 655 nm for lanthanides. Since the concentration of Arsenazo is at least 30 times higher than the concentration of the cation, complete complexation of the cation can be assumed. The extraction percentages were derived as $\%E=100\times[A^1-A/(A^1-A^0)]$, where A^0 is the absorbance of the Arsenazo solution without cation and A^1 the absorbance of the Arsenazo solution containing a known concentration of the cation before extraction.

4.4. X-ray crystallographic study

Data were collected on an STOE IPDS II two-circle diffractometer with graphite-monochromated Mo K_α radiation. An empirical absorption correction was performed using the MULABS option in PLATON.[23] The structure was solved by direct methods using the program SHELXS[24] and refined against F^2 with full-matrix least-squares techniques using the program SHELXL-97.[24] H atoms were geometrically positioned and refined using a riding model. The contribution of the disordered solvent to the scattering power had been suppressed using the SQUEEZE option in PLATON. CCDC-814605 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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